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**Modelling of Polymer Photodegradation
for Solar Cell Modules**

A Quarterly Technical Progress Report

Covering the period July 1 - September 30, 1982

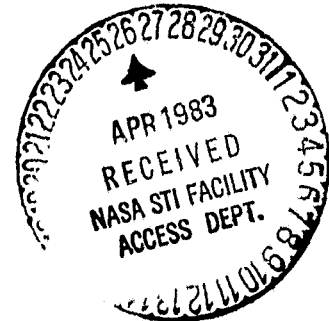
(NASA-CR-170231) MODELLING OF POLYMER
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FSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/ photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

Summary

We have developed a computer program which simulates the complex processes of photooxidation which take place in a polymer upon prolonged exposure outdoors causing it to fail in photovoltaic and other applications. The method calculates from an input data set of elementary reactions and rates the concentration profiles of all species over time.

During the past quarter we have attacked two important tasks in the program: (a) to monitor the effect of diffusion on chemical degradation and (b) to study the effect of UV stabilisers and antioxidants.

(a) THE EFFECT OF DIFFUSION ON CHEMICAL DEGRADATION

In principle, diffusion in a polymer matrix will affect the rates of all the bimolecular reactions to some degree or another. We have treated four categories of such reactions.

1. Small molecule-small molecule reaction. These reactions are

almost non-existent in the mechanism except for the addition of oxygen to small radical fragments such as the acyl radical from type I cleavage of methyl ketones. The relatively high solubility of oxygen and the mobility of these small molecules in a medium that is essentially equivalent to a very viscous liquid in local regions, minimises any special "polymer effect". The other stable small molecule product is water which may have effects on electrical properties but does not participate in the photooxidation sequence per se.

2. Small molecule-polymer "moiety" reactions. Groups formed on

the backbone of polymer chains (such as $\text{ROO}\cdot$ peroxy, RCO keto, $\text{RO}\cdot$ alkoxy, etc.) do react with "small molecule" species including oxygen and some radical fragments. The effect of the polymer medium apparently is to reduce the bimolecular collision (reaction) rates by a factor of about 10^{-2} relative to fluid solution rates, due to the reduced mobility of the chains.

3. Small molecule - polymer "solvent" reactions. Many radical reactions involve H-atom abstraction from the hydrocarbon backbone of the "solvent" polymer matrix. It is likely that all species will have C-H bonds in the immediate vicinity so that there would be no real sensitivity to diffusion and rates would then be similar to fluid solution rates.

4. Polymer "moiety"-polymer "moiety" reactions. Chemical groups formed on the backbone of polymer chains such as peroxy radicals, hydroperoxides, ketones, etc. can undergo bimolecular reactions such as disproportionation, energy transfer etc. The effect of the polymeric medium apparently is to reduce the bimolecular rates by a factor of about 10^{-4} relative to fluid solution rates, due to the reduced mobility of both reactants.

We have found that increasing the rates of all the bimolecular reactions, proportionately and together, causes a net increase in the induction time (time to failure). Figure 1 shows a linear log-log relationship for this effect. This result probably reflects the importance of the bimolecular termination of polymeric peroxy radicals which can then compete more effectively with the hydrogen abstraction propagation step, when diffusion is increased.

(b) THE EFFECT OF UV STABILISERS AND ANTIOXIDANTS

Scheme I represents the overall scheme of photooxidation and the various categories of stabilisation mechanisms. We have examined each in turn.

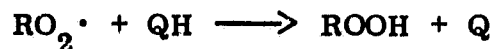
1. UV shield. Effective stabilisation of pottants or cover sheets by UV shielding would require absorption by an additive of incident radiation at wavelengths below (and only below) the visible (for colorless systems), high concentrations (several weight percent for adequate coverage), and chromophores of high extinction coefficient ($> 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in very thin films. The additive must be capable of harmlessly dissipating the substantial quantities of absorbed energy without being destroyed itself and without sensitisation of oxidation. This method is likely to be inappropriate for solar cell modules since photovoltaic conversion efficiency would be very much reduced in any case.

2. Energy transfer to quencher. We added a reaction to allow dissipation of the excited ketone with a rate constant comparable to the upper limit for a small molecule diffusion in a polymer matrix.



Figure 2 shows that up to 1 M concentration (~8%) of quencher had minimal effect on the induction time. Such a bimolecular process is just too slow for the fast unimolecular reactions of the excited ketone and stabilisation is ineffective. Again it would seem that this method per se would not be appropriate for the solar cell modules.

3. Radical trapping. Addition of a radical trap which functions much the same as in thermal oxidation by scavenging of reactive radicals has proved quite effective.



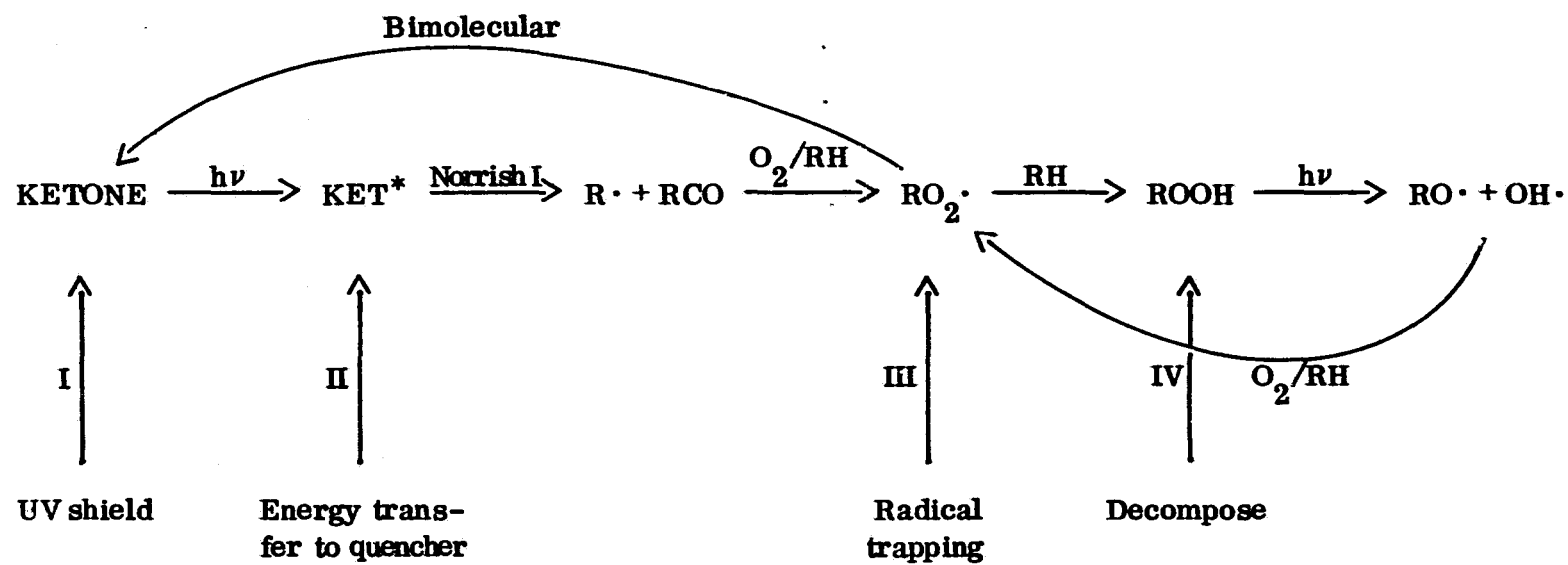
For the same value of rate constant as in (2) and for concentrations as low as 10^{-3} M, the photooxidation process was slowed. Figure 3 shows the linear dependence of the induction time as the concentration of QH is altered. Note that the trap is consumed in the process and the apparent induction time is associated with its removal. The stabilisation is less effective for higher intensity because the faster photo-or thermal-decomposition of ROOH continues the degradation process.

4. Decomposition of the hydroperoxide. Addition of the reaction



does prove effective in stabilisation since it interrupts the autocatalytic chain. Figure 2 also shows the effect on a log-log scale which is systematic but not linear.

We therefore anticipate optimum photoprotection for the encapsulant grade polymers from a combination of methods (3) and (4) above. Some nickel chelates have been known to function in both ways and ought to be considered as candidates for FSA applications. Further simulations will be continued as we attempt to approach a real life "encapsulation grade" EVA material.



Scheme I. Stabilisation mechanisms

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Figure 1. PHOTOOXIDATION OF UNSTABILIZED PE

Effect of bi(macro)molecular diffusion
(radical termination) on time to failure

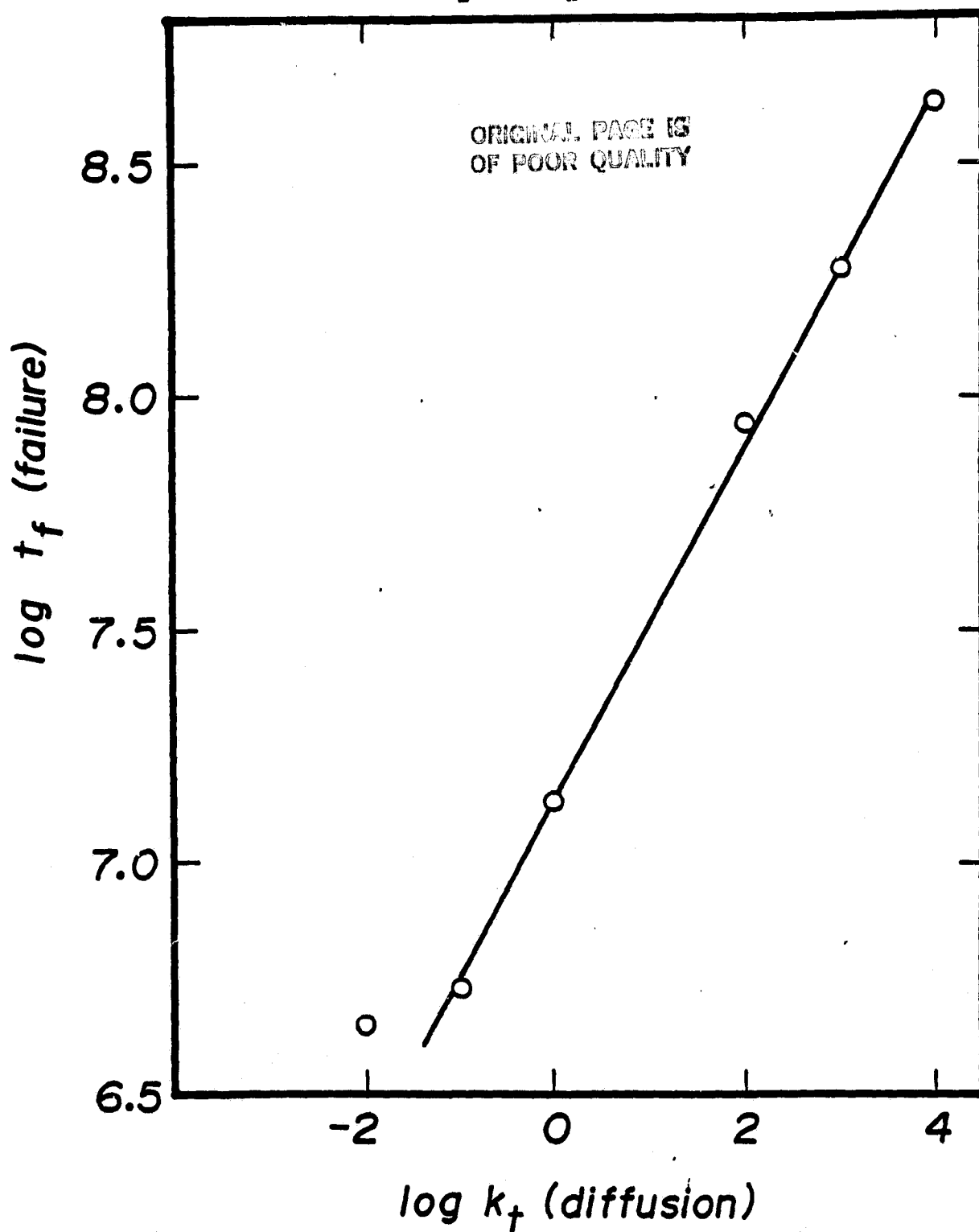
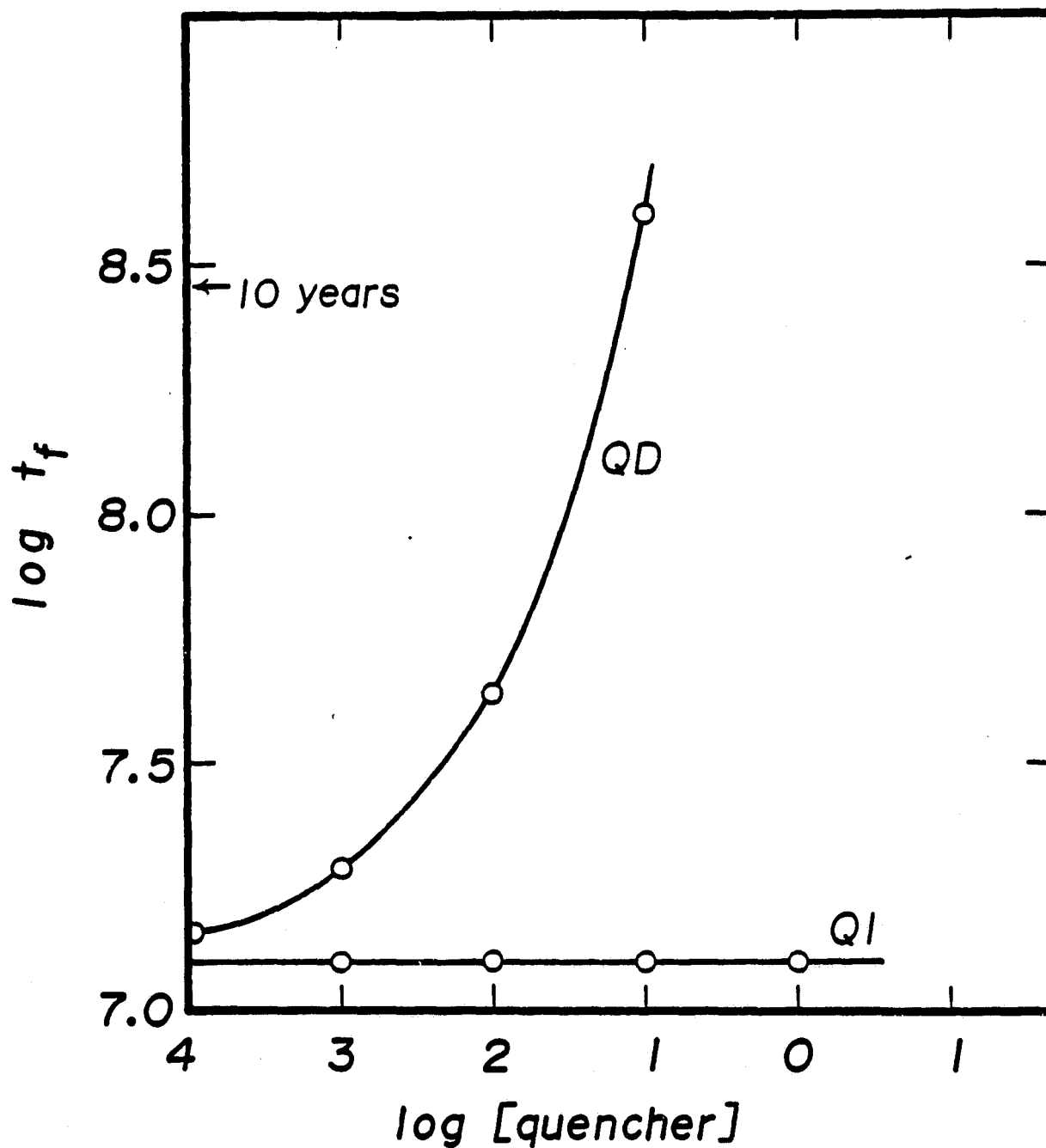
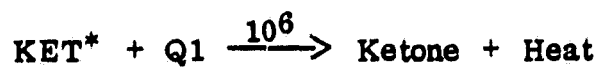
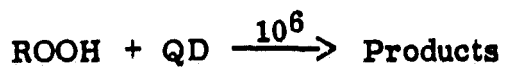


Figure 2.

STABILIZATION OF PE

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Figure 3. STABILIZATION OF PE BY RADICAL TRAPPING
(very low molecular concentration)

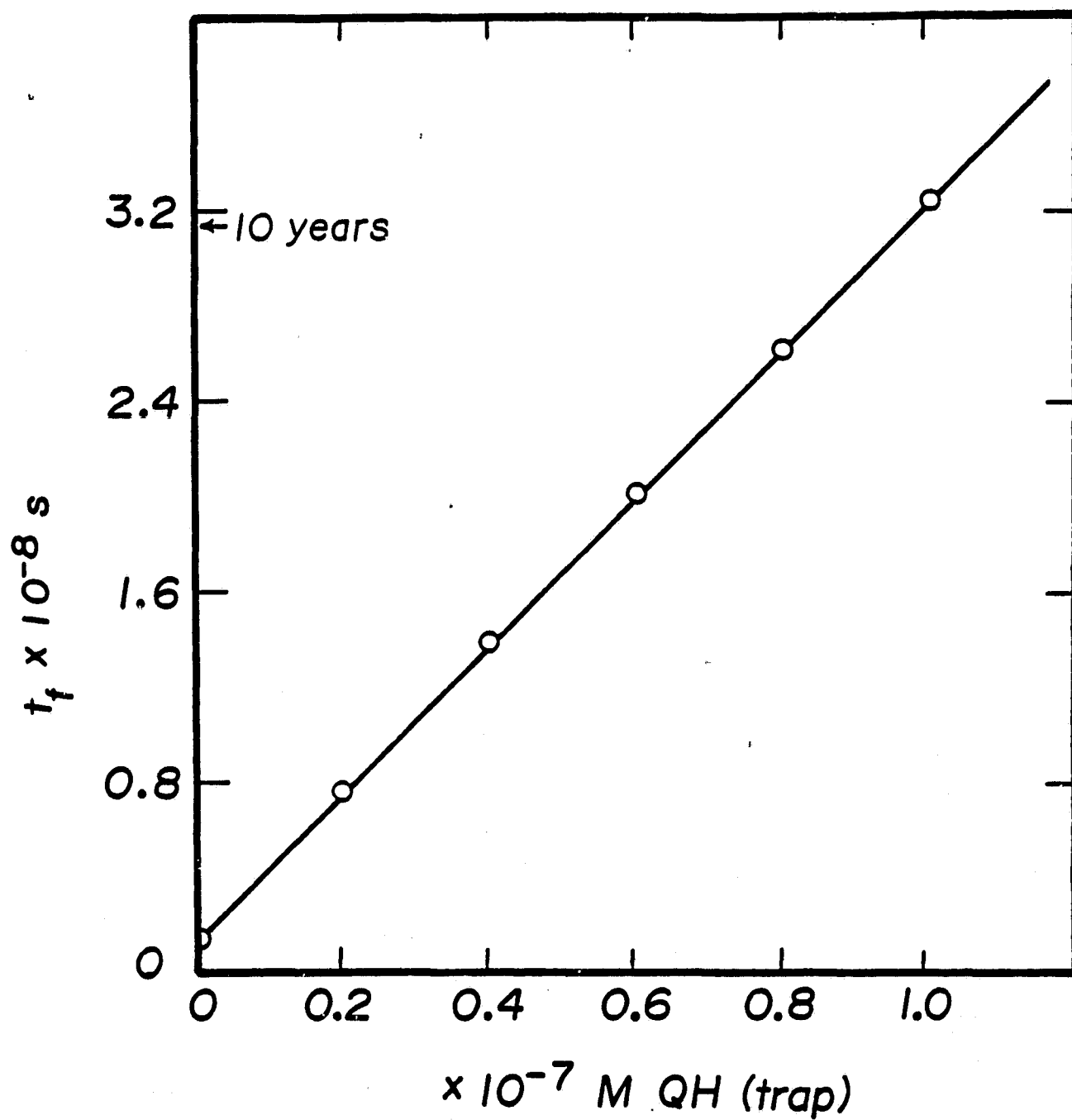
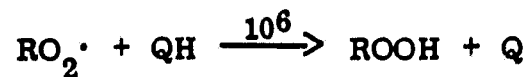


Table I. Elementary Reactions in Polymer Photooxidation
and Corresponding Rates

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Reaction	Rate constant
$RO_2 + RH \longrightarrow ROOH + RO_2$	0.1×10^{-2}
$RO_2 + RO_2 \longrightarrow ROH + Ketone + SO_2$	0.1×10^2
$RO_2 + ROH \longrightarrow ROOH + Ketone + HOO$	0.5×10^{-1}
$HOO + RH \longrightarrow HOOH + RO_2$	0.5×10^{-2}
$HOO + RO_2 \longrightarrow ROOH + SO_2$	0.1×10^8
$RO_2 + Ketone \longrightarrow ROOH + PeroxyCO$	0.5×10^{-2}
$RO_2 + ROOH \longrightarrow ROOH + Ketone + OH$	0.5×10^{-1}
$RO_2 + SMROH \longrightarrow ROOH + Aldehyde + HOO$	0.5×10^{-2}
$RO_2 + Aldehyde \longrightarrow ROOH + SMRCO$	0.1×10^3
$OH + RH \longrightarrow RO_2 + Water$	0.3×10^9
$Ketone \longrightarrow KET^*$	0.3×10^{-5}
$SMKetone \longrightarrow KET^*$	0.3×10^{-5}
$KET^* \longrightarrow SMRO_2 + SMRCO$	0.5×10^7
$SMRCO \longrightarrow SMRO_2 + CO$	0.5×10^6
$KET^* \longrightarrow Alkene + SMKetone$	0.5×10^8
$KET^* + O_2 \longrightarrow Ketone + SO_2$	0.1×10^8
$KET^* + ROOH \longrightarrow Ketone + RO + OH$	0.1×10^2
$KET^* \longrightarrow Ketone$	0.1×10^{10}
$SO_2 \longrightarrow O_2$	0.6×10^5
$SO_2 + Alkene \longrightarrow ROOH$	0.1×10^4
$SMRO_2 + RH \longrightarrow SMROOH + RO_2$	0.1×10^{-2}

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Table I (continued)

SMROOH \longrightarrow SMRO + OH	0.3×10^{-4}
SMRO + RH \longrightarrow SMROH	0.1×10^6
SMRCO + O ₂ \longrightarrow SMRCOOO	0.1×10^8
SMRCOOO + RH \longrightarrow SMRCOOOH + RO ₂	0.1×10^{-1}
SMRCOOOH \longrightarrow SMRCO ₂ + OH	0.1×10^{-3}
ROOH \longrightarrow RO + OH	0.3×10^{-4}
RO \longrightarrow SMRO ₂ + Aldehyde	0.1×10^6
RO + RH \longrightarrow RO ₂ + ROH	0.1×10^6
SMRCO ₂ + RH \longrightarrow Acid + RO ₂	0.1×10^6
RO ₂ + RO ₂ \longrightarrow ROOR	0.1×10^{-2}